



Correlation of mechanical and chemical cure development for phenol–formaldehyde resin bonded wood joints

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ARTICLE INFO

Article history:

Received 1 September 2010
Received in revised form 28 October 2010
Accepted 3 November 2010
Available online 11 November 2010

Keywords:

Dynamical mechanical analysis
Kinetic models
Phenol–formaldehyde resins
Mechanical degree of cure
Chemical degree of cure

ABSTRACT

In this study a relationship between the chemical and mechanical degree of cure (i.e. α and β , respectively) is investigated for a standard phenol–formaldehyde resin (PF). Dynamic mechanical analysis (DMA) is conducted on PF-bonded wood joints under various isothermal and linear heating regimes. Model free kinetics (MFK), viz Friedman, Vyazovkin and Kissinger–Akhira–Sunnose algorithms, are assessed for predicting the mechanical cure kinetics of PF. All MFK algorithms are found to provide a good description of PF mechanical cure. In parallel, chemical cure of the same PF samples is assessed with differential scanning calorimetry (DSC) under the same heating regimes. The relationship between chemical and mechanical degree of cure is thus obtained and observed to follow a sigmoid curve, which is best modeled with a two-parameter Weibull cumulative distribution function. The sensitivity of mechanical cure with respect to chemical cure $d\beta/d\alpha$ is also evaluated. A maximum in sensitivity is systematically observed at the vitrification point. The models developed in this study should be useful for incorporating information on the chemical and mechanical cure kinetics of adhesives in hot-pressing models and other processing models.

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1. Introduction

Modeling and optimizing of wood-based composite manufacture is playing a larger role in design of processes and manufacturing equipment. In these models, internal temperature and moisture conditions are computed with an aim towards predicting when polymeric cure is sufficient to avoid delamination at the time of press opening. In order to incorporate cure kinetics into a comprehensive hot-pressing model for fully describing thermodynamic, curing, and rheological processes, it is necessary to find a suitable model for describing the kinetics of cure for wood adhesives. Phenol–formaldehyde (PF) resins are common adhesives for wood-based panels. During cure PF prepolymers develop into a crosslinked network that confers high mechanical strength and durability to the final product; most kinetic studies of PF resins are based on data from differential scanning calorimetry (DSC) where model free kinetics have been found to best describe the development of chemical cure [1–4]. However, mechanical cure can also be monitored by dynamic mechanical analysis (DMA) for example and can also be described with traditional kinetic models. The n th order models have been proposed for describing mechanical

cure development as measured by storage modulus in DMA [5,6]. In contrast model-free kinetics such as the Kissinger–Akhira–Sunnose (KAS), Friedman and Vyazovkin methods which are well suited for describing chemical cure with DSC data have not been assessed on DMA data [7].

Heat evolution in DSC is typically assumed to be proportional to the formation of a chemical network during polymerization [8], but how mechanical properties relate to chemical bond formation remains unknown. In fact, the kinetics of chemical advancement of the adhesive layer is not necessarily linearly related with the developing rate of mechanical properties. Some studies have shown that the cure development derived from storage modulus E' (defined as mechanical cure) was not in agreement with that derived from reaction heat by DSC (defined as chemical cure) [9]. Mechanical cure as measured with DMA appears to complete earlier than chemical cure as measured with DSC [10,11]. Others have reported for an advanced plywood PF, a good agreement between stiffness development in torsional braid analysis and thermal events in DSC [12]. In general it is clear that the relationship between chemical and mechanical advancements remains ambiguous and undefined; however, both are needed to describe bondline development completely for thermosetting resins such as phenolics.

Understanding cure kinetics and mechanical property development in wood/adhesive systems is important for evaluating adhesive performance, formulating new resins, and optimizing

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process parameters. In this perspective, the objectives of this research are to: (1) evaluate the applicability of model-free kinetics for describing the mechanical cure development of phenolic resins in DMA and (2) explore and model the relationship between mechanical cure from DMA and chemical cure from DSC on a same adhesive.

2. Experimental

2.1. PF resin

A PF resole resin, tailored as an adhesive for the core layer of oriented strand boards, was obtained from Georgia-Pacific Company, frozen and stored at -20°C until use. The resin had a high molecular weight with an $M_w = 5576\text{ g/mol}$ and $M_w/M_n = 1.72$. The resin solid content was 45.0% with 3.7 wt% nitrogen, indicating the presence of urea [7].

2.2. DMA specimen preparations

Planed basswood strips (Midwest Products Inc.) with nominal dimensions of $50\text{ mm} \times 12\text{ mm} \times 1\text{ mm}$ were oven-dried at 103°C and stored in a desiccator over anhydrous calcium sulfate until use. Sandwich-type DMA specimens were produced from a layer of PF resin between two pieces of wood adherends. Care was taken to match the grain, thickness, and weight of the two wood adherends within the specimen to maintain a balanced composite design. The bonding surfaces were lightly hand sanded along the grain with 220-grit sandpaper and cleaned with a paper towel immediately prior to resin application. The resin was uniformly applied to the prepared surface of both wood adherends using a small airbrush (BADGER Model 350). The amount of resin solid applied to each surface was set at ca. 50 g/m^2 , which equates to ca. 12% of dried wood mass.

Maintaining a consistent resin content was deemed important to repeated cure analysis. He and Yan [13] demonstrated that the degree of resin loading can influence the cure development. They concluded that this influence occurred primarily through water absorption and evaporation during the DMA test. Therefore, the specimens were wrapped with thin aluminum foil to maintain moisture content during the tests for the DMA and allow comparable conditions to those used in the DSC with sealed crucibles [14].

DMA measurements were conducted on the sandwich specimens in three-point bending mode at a span of 25 mm with a Tritec 2000 analyzer (Triton Technology). The frequency was fixed at 1 Hz. Strain sweep tests were conducted to establish the linear viscoelastic ranges at working temperature. Oscillation displacement amplitude of 0.03 mm was thus chosen. DMA was performed isothermally at 90, 100, 110, 120, 130, 140, and 160°C with triplicates at each temperature. In each test, the DMA oven was preheated to the predetermined isothermal temperature, and then the specimen was installed quickly and held at the cure temperature until both modulus and damping approached a constant value signifying the completion of detectable mechanical cure. In addition, ramp experiments were performed at heating rates of 1, 2, 3, 4, and 5°C/min from room temperature to 250°C with triplicates at each heating rate. Low heating rates were selected to make sure that the effect of thermal lag was minimal.

2.3. DSC

To determine the relationship of cure development by DMA and DSC, a Mettler-Toledo DSC 822e was used to scan a sample of resin trimmed from the DMA specimens immediately following DMA sample preparation. To do so, small disks were sampled from the

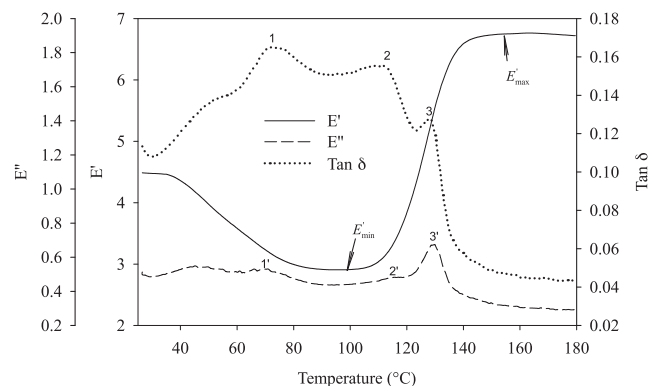


Fig. 1. Typical DMA traces at 2°C/min for flexural storage modulus E' (GPa), loss modulus E'' (GPa), and loss factor $\tan \delta$. Numbers (1, 2, and 3 on $\tan \delta$; 1', 2' and 3' on E') indicate the glass transition temperature of uncured PF resin, cure transition of gelation and vitrification points; respectively.

DMA specimens with a paper hole puncher and placed into $30\ \mu\text{l}$ high pressure gold-plated crucibles. In that way the resin could be described in terms of mechanical cure but also in terms of chemical cure with the DSC since samples for DSC and DMA came from the same preparation. Ramp temperature scans were conducted at 5 heating rates 2, 3, 4, 5, 10, and 15°C/min from 25 to 240°C . The chemical cure development was obtained under linear heating rates and isothermal chemical cure development was predicted with ramping data as described by Wang et al. [7].

3. Results and discussion

3.1. Characterization of mechanical cure

The representative changes for E' and $\tan \delta$ with temperature are presented in Fig. 1 for a typical PF-bonded wood joint cured at 2°C/min and have been discussed in detail in a previous publication [14]. Three distinct zones are observed from E' curve: thermal softening of the uncured wood–resin system, resin curing, and thermal softening of the cured wood–resin system. Upon application of the liquid PF resin to the dry wood surface, water is absorbed by the wood causing the adhesive layer to become semi-solid at room temperature. In this state, the adhesive can transfer partial shear forces between two pieces of wood. With increasing temperature, the resin–wood system gradually softens and the E' decreases reaching a minimum E' plateau. This event appears on $\tan \delta$ curve as the first peak centered at ca. $50\text{--}70^{\circ}\text{C}$ (Fig. 1). It may be ascribed to the glass transition temperature (T_g) of the uncured PF resin or to wood lignin that is known to soften in this temperature range when plasticized [15]. At this point, the E' reaches a minimum plateau corresponding to a competitive relationship between the resin softening and curing during the heating process. With the subsequent increase in E' , the resin cure begins to outpace the softening. For convenience, this point (E'_{\min}) is defined here as the onset of the mechanical cure ($\beta=0$). Shortly after E'_{\min} , a second peak is evident in $\tan \delta$. This second peak is taken to be the gelation point, where the reaction has progressed to form an infinite molecular weight network [5,16]. When only a single peak is evident in the $\tan \delta$ curve, gelation is defined as the temperature corresponding to the onset of increase in E' [13]. Finally, the third peak in the $\tan \delta$ curve is defined as the vitrification point, i.e. the attainment of the glassy state as the T_g of the forming polymer reaches the cure temperature [5,16]. A maximum in modulus is then attained, E'_{\max} . At higher temperatures E' slightly decreases, possibly due to the thermal softening of the cured resin or progressive degradation of wood substrate as well as differential expansion between resin and wood [17]. Subsequently, the degree of mechanical cure can be defined

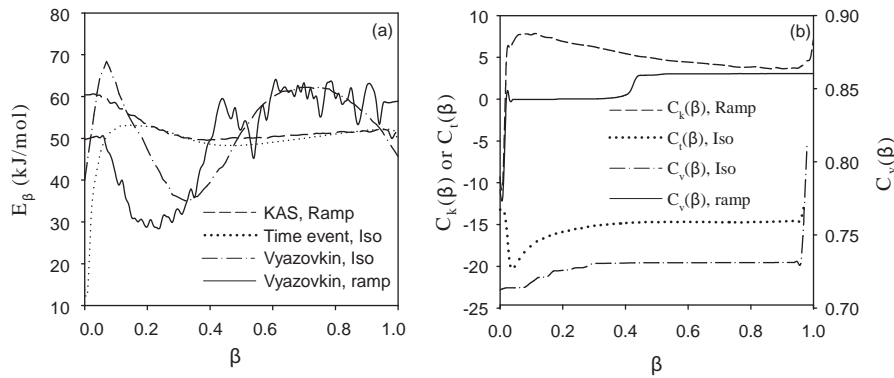


Fig. 2. Activation energy dependence of mechanical cure (a) and combined parameters (b) obtained by KAS, Time Event, and Vyazovkin methods for PF-bonded wood joints under isothermal and ramp cure regimes.

as [6].

$$\beta = \frac{E'(t) - E'_{\min}}{E'_{\max} - E'_{\min}} \quad (1)$$

where E'_{\min} , E'_{\max} , and $E'(t)$ are the minimum, maximum E' , and at the time t during cure processes; respectively.

3.2. Model-free kinetics of the mechanical cure development

The basic assumption of the model-free methods is that activation energy is dependent on the development of the reaction [18,19]. The MFK Friedman, KAS and Time Event algorithms are common methods [20] to describe the activation energy dependence on the advancing degree of cure for phenolic resins. The basic kinetic model formulated for β is:

$$\frac{d\beta}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\beta) \quad (2)$$

The direct use of Eq. (2) gives rise to the differential method of MFK Friedman ((3)) that could be applied to isothermal as well as to ramp data [7,21].

$$\ln\left(\frac{d\beta}{dt}\right)_{\beta_i} = C_f(\beta) - \frac{E_\beta}{RT_{\beta_i}} \quad (3)$$

where $C_f(\beta)$ and E_β are MFK Friedman complex parameter and activation energy; respectively (subscripts β and i refer to specific mechanical degree of cure and a series of heating regimes hereafter). For isothermal conditions, integration and rearrangement of Eq. (2) yields:

$$\ln(\Delta t_{\beta_i}) = \ln\left(\frac{g(\beta)}{A_\beta}\right) + \frac{E_\beta}{RT_i} \quad (4)$$

where $g(\beta) = \int_0^\beta d\beta/f(\beta)$ is the integral form of the reaction model $f(\beta)$ and Δt_{β_i} is the time required to reach a specified conversion, β , at an iso-temperature, T_i . Let $C_t(\beta) = \ln(g(\beta)/A_\beta)$, then E_β and $C_t(\beta)$ was evaluated from the slope and intercept of the plot $\ln \Delta t_{\beta_i}$ against reciprocal of temperature $1/T_i$. This method was thereafter referred as the Time Event model-free kinetics [20].

For ramp conditions, the model-free KAS method uses Eq. (5) [22,23].

$$\ln\left(\frac{\varphi_i}{T_{\beta_i}^2}\right) = C_k(\beta) - \frac{E_\beta}{RT_{\beta_i}} \quad (5)$$

where φ_i indicates a series of ramp rates, °C/min; likewise, the model-free Vyazovkin method can be applied to isothermal and ramp data to obtain two set of parameters. In the Vyazovkin method, n scans are performed at different heating regimes $T(t)$.

The activation energy at a specific degree of cure is obtained by minimizing the function $\varphi(E_\beta)$ [1]:

$$\varphi(E_\beta) = \sum_{i=1}^n \sum_{j=1}^n \frac{I[E_\beta, T_i(t_\beta)]}{I[E_\beta, T_j(t_\beta)]} \quad (j \neq i) \quad (6)$$

In Eq. (6) the temperature integral, I , is defined as:

$$I[E_\beta, T(t_\beta)] = \int_{t_\beta - \Delta\beta}^{t_\beta} \exp\left(\frac{-E_\beta}{RT(t)}\right) dt \quad (7)$$

And $C_v(\beta)$ is defined as

$$C_v(\beta) = \int_0^\alpha \frac{d\beta}{A f(\beta)} = \frac{1}{\varphi} \int_{T_0}^T \exp\left(\frac{-E_\beta}{RT}\right) dt \quad (8)$$

Fig. 2a depicts the activation energy curves for PF-bonded wood joints. The parameters are calculated from isothermal data using the Time Event [20] and Vyazovkin methods, from ramp data by the KAS, Friedman and Vyazovkin methods [7]. The first observation from Fig. 2a is that all the methods provide on average similar activation energies. For example the Vyazovkin and Time Event methods from isothermal data give E_a of 53 and 49 kJ/mol, respectively; from the ramp data by Vyazovkin, Friedman and KAS methods we calculate 50, 49 and 52 kJ/mol. All MFK methods are therefore in general agreement. As Wang et al. [7] demonstrated for DSC data, the activation energy curves overlapped when computed by the Friedman and the Vyazovkin methods for the DMA data. To simplify the graphs, the activation energy curves by the Friedman method are not plotted in Fig. 2a. It was observed that the activation energy computed from ramp data by the KAS method nearly overlapped with that from isothermal data by Time Event method. The most notable exceptions are at a low degree of cure. In this case, the activation energy obtained from both ramp and isothermal data with the Vyazovkin method followed a similar pattern. The MFK combined parameters $C(\beta)$ are shown in Fig. 2b. Their physical meanings are not obvious but together with activation energy they fully describe cure development and allow cure predictions under any regime.

The approach for predicting cure development from these parameters has been explained in a former publication and was also used in this study from the DMA data [7]. These algorithms were computed for DMA data. The parameters by Vyazovkin obtained from isothermal data can be used to predict cure behavior under isothermal temperature in the same manner as the Vyazovkin method from ramp data. With the MFK Time Event method, substituting the parameters E_β and $C_t(\beta)$ into Eq. (4), the time needed to reach a specific β can be obtained at specific isothermal tempera-

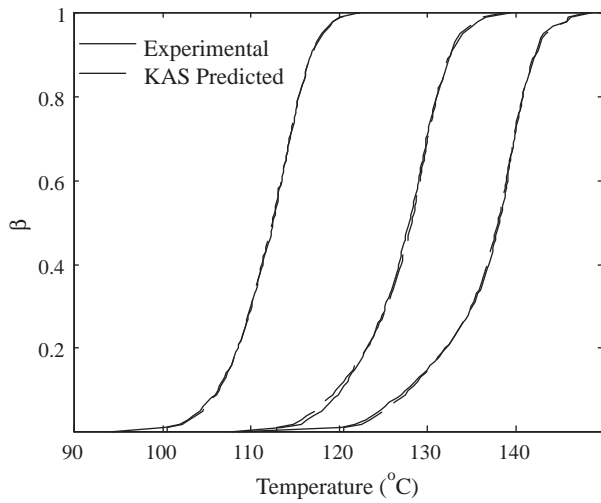


Fig. 3. Comparison of experimental mechanical degree of cure at 1, 2, and 3 °C/min for PF-bonded wood joints and KAS predictions from ramp data.

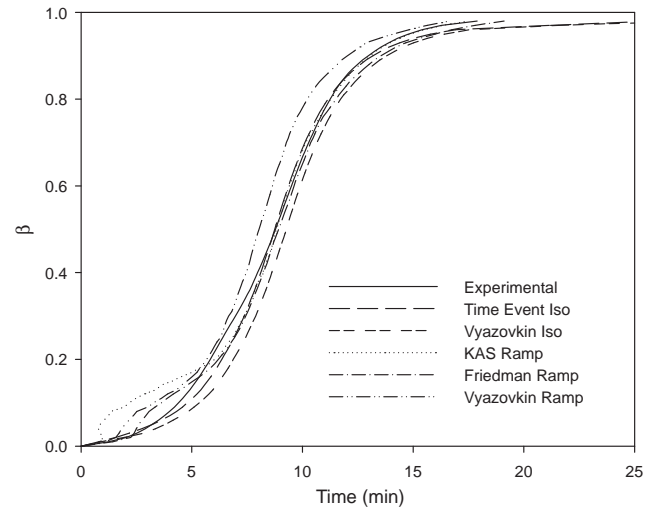


Fig. 4. Comparison of experimental mechanical degree of cure at 120 °C for PF-bonded wood joints and predictions with parameters E_β and $C(\beta)$ from ramp and isothermal data.

ture. The KAS predictions at various heating rates are compared to experimental data in Fig. 3 while Fig. 4 shows the experimental data at 120 °C and predictions by KAS, Friedman and Vyazovkin methods from ramp data (KAS Ramp, Friedman Ramp, and Vyazovkin Ramp) and by Time Event and Vyazovkin methods from isothermal data (Time Event Iso and Vyazovkin Iso). Predictions were calculated with these kinetic parameters so as to predict the cure time needed to achieve a specific degree of cure at a given temperature. The root mean square error was the root of average squared difference between real experimental data and the model predicted data. The smaller the root mean squared error, the closer the fit is to the experimental data. The cure time was around 18 min at 120 °C. Relative to this time scale, all models appeared to adequately predict mechanical cure. This was confirmed by the small root mean square

errors of prediction with 1.0 min for Time Event Iso, 1.3 min for Vyazovkin Iso, 0.8 min for KAS Ramp, 0.5 min for Friedman Ramp, and 0.8 min for Vyazovkin Ramp.

3.3. Relationship between mechanical cure and chemical cure

In order to investigate the relationship of mechanical degree of cure with chemical degree of cure, the chemical cure kinetics was obtained by DSC with small discs taken from fresh DMA samples. The evolution of α at linear heating rates (Fig. 5a) was determined by the Mettler-Toledo DSC STARE software. Due to difficulty and accuracy problems of the isothermal DSC scans [7], the evolution at isothermal temperature (Fig. 5b) was predicted according to the model-free Vyazovkin method with parameters from ramp data

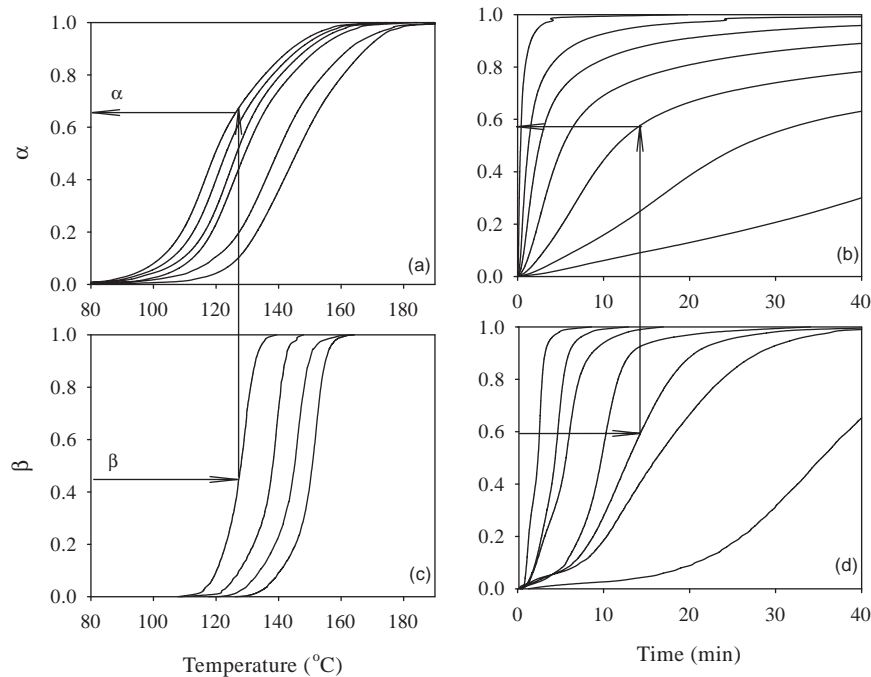


Fig. 5. The evolution of degree of cure at different cure conditions: (a) chemical cure by DSC at 2, 3, 4, 5, 10, and 15 °C/min from left to right, (b) predicted chemical cure at isothermal temperature 90, 100, 110, 120, 130, 140, and 160 °C bottom up by Vyazovkin model-free kinetics from DSC ramp data in (a) [7], (c) mechanical cure by DMA at 2, 3, 4, and 5 °C/min from left to right for PF-bonded wood joints, and (d) mechanical cure by DMA at 90, 100, 110, 120, 130, 140, and 160 °C bottom up for PF-bonded wood joints.

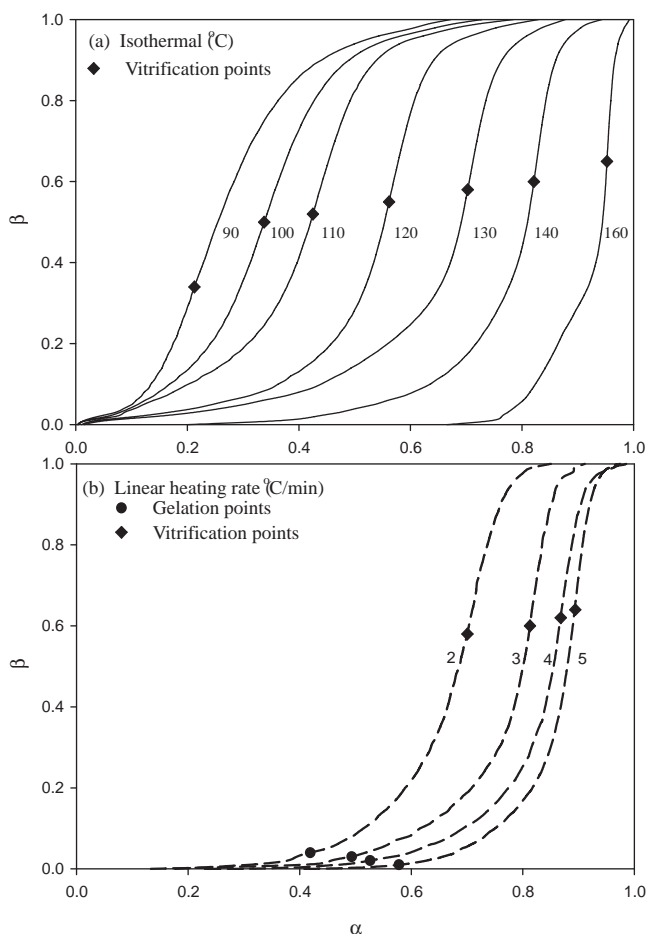


Fig. 6. Relationship between mechanical cure (β) and chemical cure (α) from PF-bonded wood joints under isothermal temperatures (a) and linear heating rates (b).

[7]. By comparing α to the prevailing time or temperature with the corresponding β (as shown by arrows in Fig. 5), the relationship between chemical cure and mechanical cure was obtained in Fig. 6. It was observed that the mechanical cure changed with chemical cure following a sigmoid.

Under both isothermal and linear heating regimes, a comparison of mechanical cure with chemical cure shows three stages: (1) an induction period at low conversion, where mechanical cure does not increase much with chemical cure; (2) a rapid increase in mechanical properties with medium to high levels of α ; (3) a decreasing rate of mechanical property development leading to a cessation of mechanical cure. At low isothermal temperatures, the onset of mechanical cure is almost identical to the onset of chemical cure; however the sensitivity of mechanical cure development at the early stages of chemical cure is low. For these conditions, the cessation of mechanical cure occurs at a low chemical cure of around 0.6. With increasing isothermal temperature, the onset of mechanical cure is delayed until much higher chemical cure. For example at 160 °C cure temperature, the mechanical cure does not start until a chemical degree of cure of 0.7 and mechanical cure ceases close to full chemical cure. These observations indicate that the initial stages of chemical cure do not increase viscosity or shear modulus proportionally. In addition, when the curing temperature is high, the resin needs to attain substantial chemical cure to resist the softening effects of temperature. The mechanical stiffness is influenced by both chemical advancement and curing regime as for example a higher degree of chemical cure is required to achieve an equivalent modulus observed at a lower temperature. Hence, the

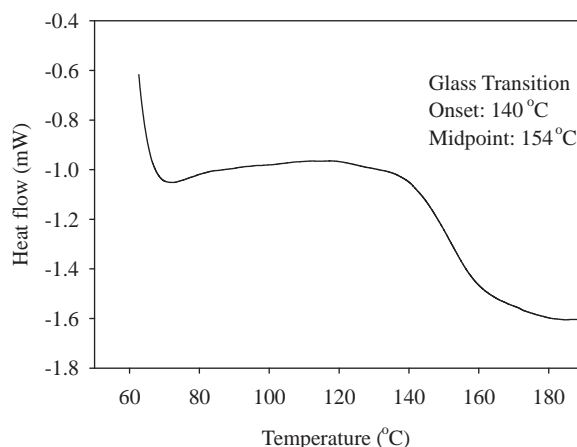


Fig. 7. DSC thermogram at 10 °C/min showing glass transition temperature for a sample with two small pieces of basswood discs bonded by PF, trimmed from the DMA specimen after being scanned from room temperature to 240 °C at 5 °C/min.

cure curve shifts to the higher degree of chemical cure as the cure temperature increases. The wood/PF system has a T_g around 154 °C as measured under ramp heat rate at 5 °C/min by DSC (Fig. 7).

From these data, one can also extract the β and α at the gelation and vitrification points (Table 1). As expected gelation roughly corresponds with the onset of mechanical cure. It has been reported that gelation occurs at a constant conversion for a given thermoset, independently of cure regimes [8]. In this study, the average value of α at gelation is ca. 0.50 and it systematically increases with heating rates (Table 1). Other researchers have reported a similar behavior and ascribed the non-iso-conversional character of gelation to the heterogeneity of the curing process [9,24]. Similarly α at the vitrification point increases with heating rate or isothermal temperature as expected and observed on other thermosets [11].

To mathematically model the relationship between β and α , a two-parameter Weibull cumulative distribution function was fitted

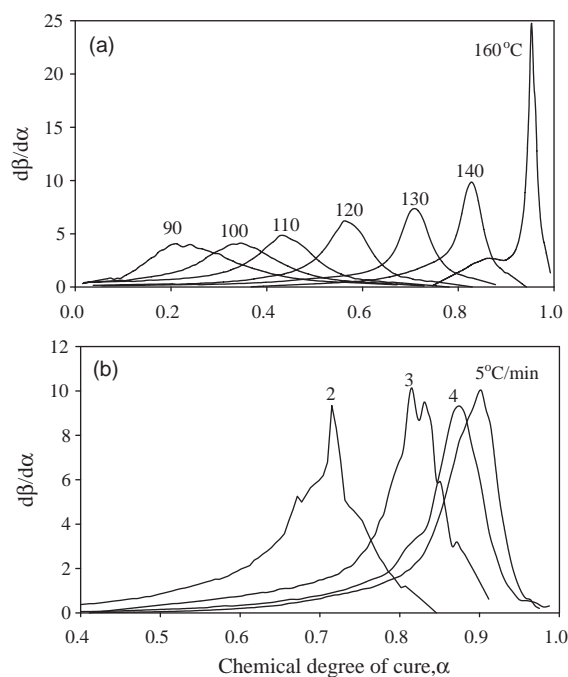


Fig. 8. Sensitivity of mechanical property development to chemical advancement at designated isothermal temperature and linear heating rates computed from experimental data.

Table 1

Mechanical and chemical degrees of cure at the gelation and vitrification points under the linear and isothermal heating regimes for PF-bonded wood joints.

| | | Ramp (°C/min) | | | | Iso temperature (°C) | | | | | | |
|---------------|----------|---------------|------|------|------|----------------------|------|------|------|------|------|------|
| | | 2 | 3 | 4 | 5 | 90 | 100 | 110 | 120 | 130 | 140 | 160 |
| Gelation | β | 0.04 | 0.03 | 0.02 | 0.01 | | | | | | | |
| | α | 0.42 | 0.49 | 0.52 | 0.57 | | | | | | | |
| Vitrification | β | 0.58 | 0.60 | 0.62 | 0.64 | 0.34 | 0.50 | 0.52 | 0.55 | 0.58 | 0.60 | 0.65 |
| | α | 0.7 | 0.81 | 0.87 | 0.89 | 0.22 | 0.34 | 0.43 | 0.56 | 0.7 | 0.82 | 0.95 |

Table 2

Parameters for the relationship equation of mechanical and chemical cure.

| | Isothermal temperature (°C) | | | | | | | Linear heating rate (°C/min) | | | | |
|-----|-----------------------------|------|------|------|------|-------|-------|------------------------------|-------|-------|-------|--|
| | 90 | 100 | 110 | 120 | 130 | 140 | 160 | 2 | 3 | 4 | 5 | |
| k | 3.35 | 2.67 | 2.22 | 1.74 | 1.41 | 1.22 | 1.05 | 1.42 | 1.23 | 1.15 | 1.13 | |
| m | 2.60 | 3.43 | 4.53 | 7.55 | 9.24 | 14.33 | 25.71 | 9.74 | 14.74 | 15.68 | 19.06 | |

 $R^2 > 0.99$ for all fitting parameters.

to the experimental data (Eq. (9)).

$$\beta = 1 - \exp(-(k\alpha)^m) \quad (9)$$

$$\frac{d\beta}{d\alpha} = km(k\alpha)^{m-1} \exp(-(k\alpha)^m) \quad (10)$$

where k and m are fitting parameters obtained with nonlinear regression with R -square larger than 0.99. Both parameters were found to depend on the isothermal cure temperature or heating rate (Table 2).

The sensitivity of β to changes in α , defined by $d\beta/d\alpha$ can then easily be computed from (10). Experimental data of $d\beta/d\alpha$ (Fig. 8) under isothermal heating regime and linear heating regime show that the dependence of β on α goes through a maximum corresponding to $(k\alpha)^m = (m-1)/m$. The value of α at this maximum development of mechanical property with respect to chemical cure coincides with vitrification, as one would expect; i.e. in the vicinity of the vitrification point, small changes in chemical advancement promote a large mechanical increment.

4. Conclusion

The mechanical cure development as detected from storage modulus increase in a DMA cure test of phenolic bonded sandwiches was modeled by model-free kinetics. The activation energies dependence on mechanical degree of cure was obtained by various model-free kinetic methods and the predictions from all algorithms were good and in agreement with each others. The chemical cure kinetics of the same samples were also determined from DSC measurements under similar conditions. This allowed correlating the mechanical and chemical degrees of cure for PF-bonded wood joints. Mechanical cure was found to follow a sigmoid relation with chemical cure in accordance with a two-parameter Weibull cumulative distribution function. The chemical degree of cure at the gelation points and at vitrification points increased with isothermal temperature or linear heating rates. Sensitivity of mechanical cure development with respect to chemical cure ($d\beta/d\alpha$) was also revealed and a maximum point of sensitivity was found to coincide with vitrification. With the approach and models developed, one can now estimate and relate mechanical and chemical cure kinetics from one another. Such models should be useful for the development of accurate hot-pressing models of wood-based composites which would encompass all information about the resin hardening.

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